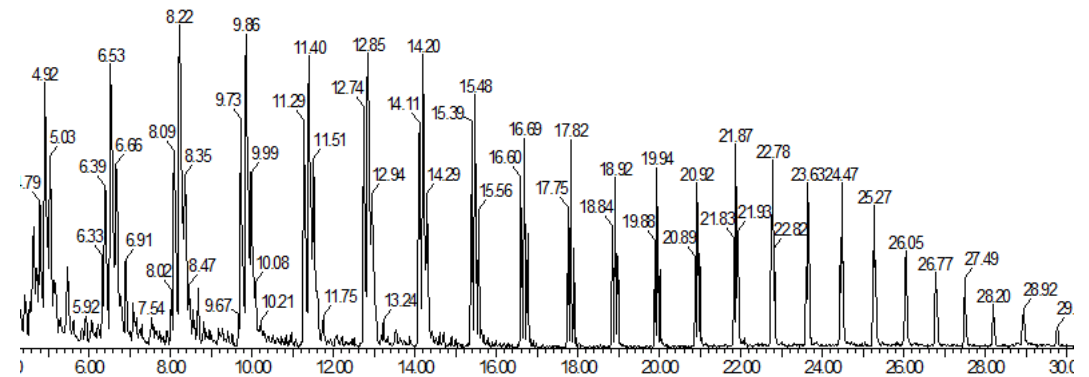


# *Microplastics identification by pyrolysis gas chromatography mass spectrometry (py-GCMS)*

Presented by John W Scott, ISTC Senior Analytical Chemist



Polyethylene

# Plastic -Designed to Last Forever, Yet Intended for Single Use

1



## Throwaway Living

DISPOSABLE ITEMS CUT DOWN HOUSEHOLD CHORES

- Cumulative plastic waste generated is 6.3 billion metric tons<sup>1</sup>.
- 79% of this material deposited in landfills and the natural environment<sup>1</sup>.
- Microplastics are now ubiquitous in the environment.
- Models predict that 50% of the plastics found in European seas are more than 17 years of age<sup>2</sup>.



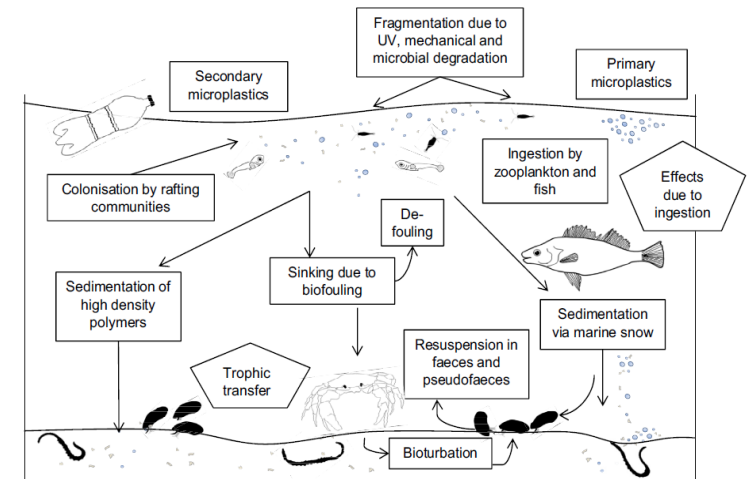
1 - Geyer, Roland, Jenna R. Jambeck, and Kara Lavender Law. "Production, use, and fate of all plastics ever made." *Science advances* 3, no. 7 (2017): e1700782.

2- Koelmans, Albert A., Adil Bakir, G. Allen Burton, and Colin R. Janssen. "Microplastic as a vector for chemicals in the aquatic environment: critical review and model-supported reinterpretation of empirical studies." *Environmental science & technology* 50, no. 7 (2016): 3315-3326.

# The Impact of Environmental Plastics

2

- Adverse effects on humans and wildlife currently under investigation. Some studies show neutral effects, others show negative effects<sup>3</sup>.
- Vectors for chemical exposure to POPs, emerging contaminants, etc.
- Vectors for pathogens and viruses.
- Economic losses in tourism and fisheries<sup>4,5</sup>.
- Identification of the materials present in the environment is important for source appointment, risk assessment, abatement and wildlife management



Wright, S. L., R. C. Thompson, and T. S. Galloway. 2013. The physical impacts of microplastics on marine organisms: A review. *Environmental Pollution* 178:483–492.



3- Foley, Carolyn J., Zachary S. Feiner, Timothy D. Malinich, and Tomas O. Höök. "A meta-analysis of the effects of exposure to microplastics on fish and aquatic invertebrates." *Science of the Total Environment* 631 (2018): 550-559.

4- Mouat, J., Lozano, R. L. & Bateson, H. (2010). *Economic Impacts of marine litter*. KIMO International, pp. 105.

Beaumont, Nicola J., Margrethe Aanesen, Melanie C. Austen, Tobias Börger, James R. Clark, Matthew Cole, Tara Hooper, Penelope K. Lindeque, Christine Pascoe, and Kayleigh J. Wyles. "Global ecological, social and economic impacts of marine plastic." *Marine Pollution Bulletin* 142 (2019): 189-195.



# Identification of Microplastics

FT-IR Microscope



pyGCMS



## Versus

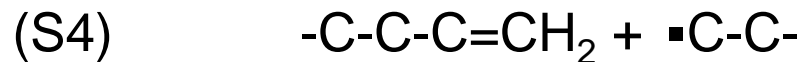
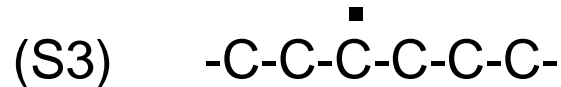
- Short Analysis Time (Minutes)
  - Can analyze samples directly on filter
  - Analysis is Non-Destructive
  - Can be problematic with small sample sizes
  - Difficulty with some materials (i.e. rubbers)
  - Limited information
- Long Analysis Time(~ 1 hour)
  - Samples have to be removed from filters
  - Destructive
  - Can analyze small samples (100  $\mu\text{g}$  or less)
  - Can detect a wider range of materials
  - More detailed information

# Analytical Pyrolysis – The Theory Behind the Technique

4

## Degradation Mechanisms

- Random Scission – Example Polyolefin



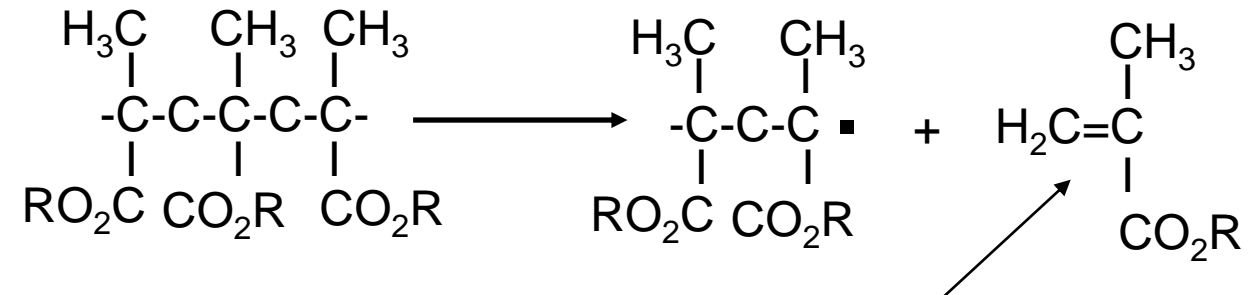
Major products – Hydrocarbons (saturated, with one terminal double bond, and with two terminal double bonds)

- Side Group Scission – Example polyvinyl chloride



Major products – Aromatics (benzene, toluene, naphthalene) and chlorinated aromatics.

- Monomer Reversion– Example poly(methyl methacrylate)



Major products – Methyl methacrylate

# pyGCMS - Instrumentation

Load Material in Quartz Capillary Tube



Separate products with GC



Transfer Line

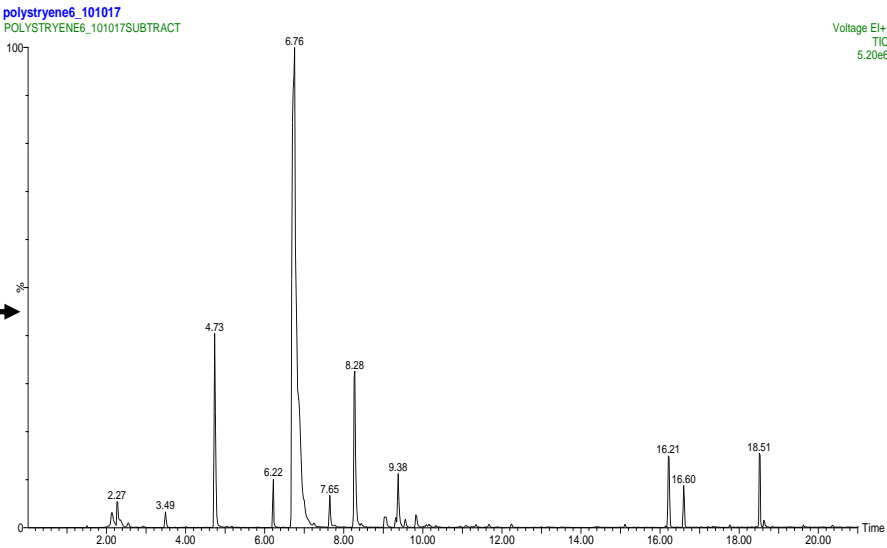


Pyrolysis products

Detection by Mass Spectrometry



Pyrogram

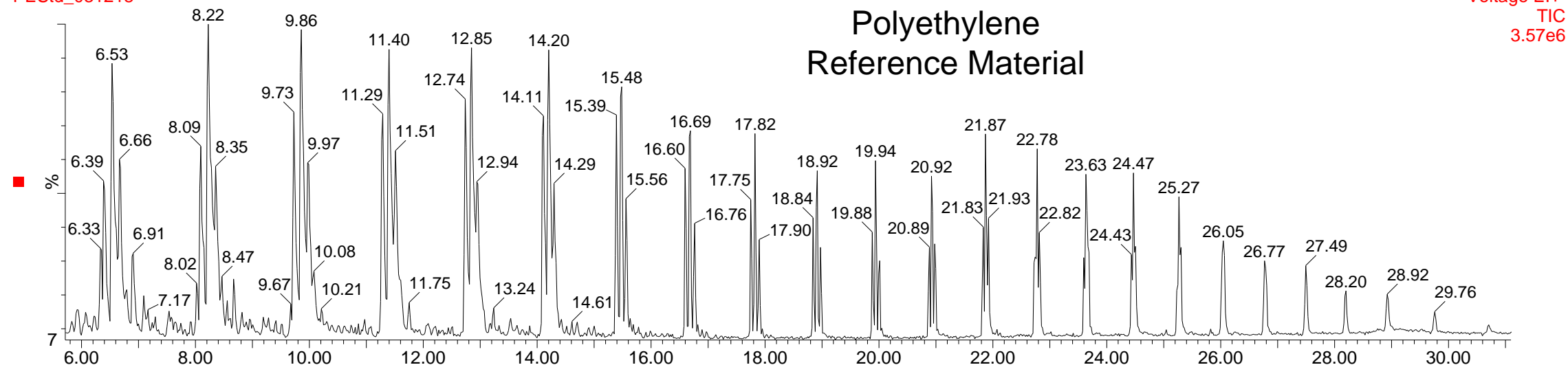


# Karst Water – Microplastic Pyrogram

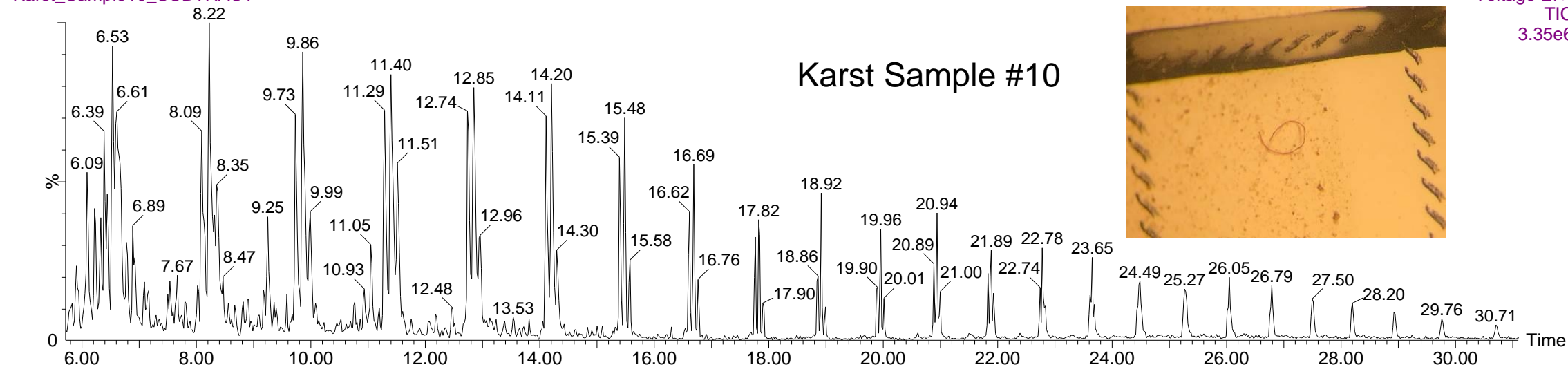
6

PEStd\_031218

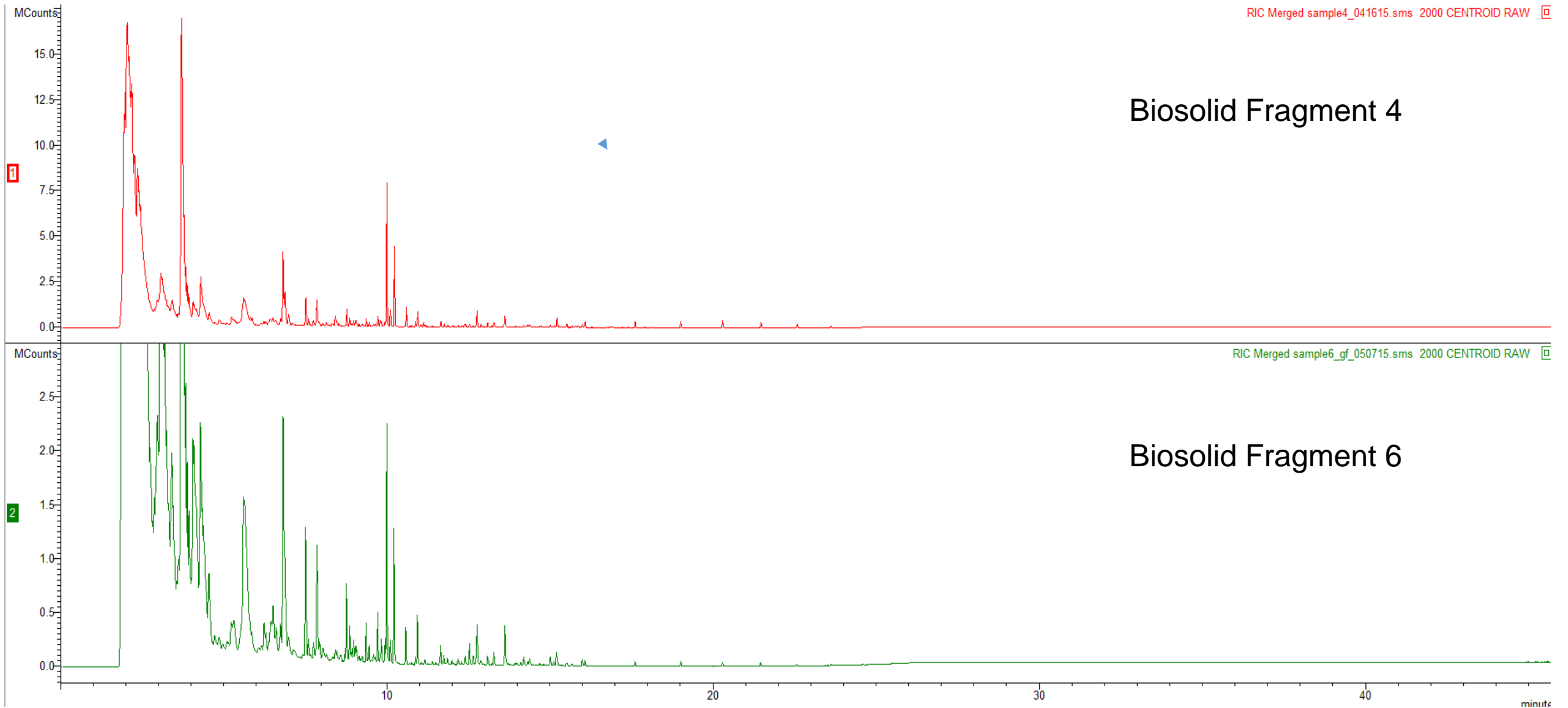
PEStd\_031218



Karst\_Sample10\_SUBTRACT



# Biosolids– Microplastic Fragments





# Biosolids– Microplastic Fragments

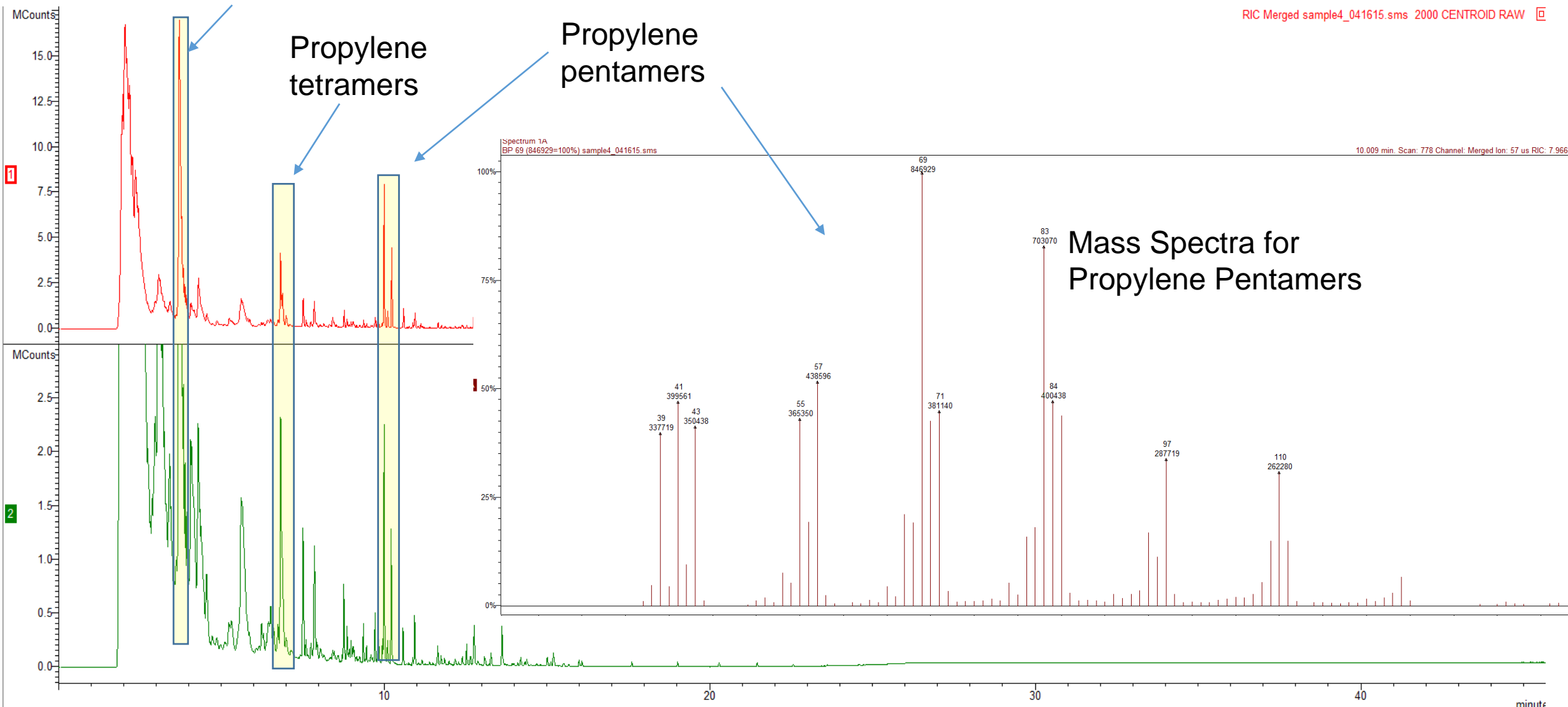
8

Propylene  
trimer

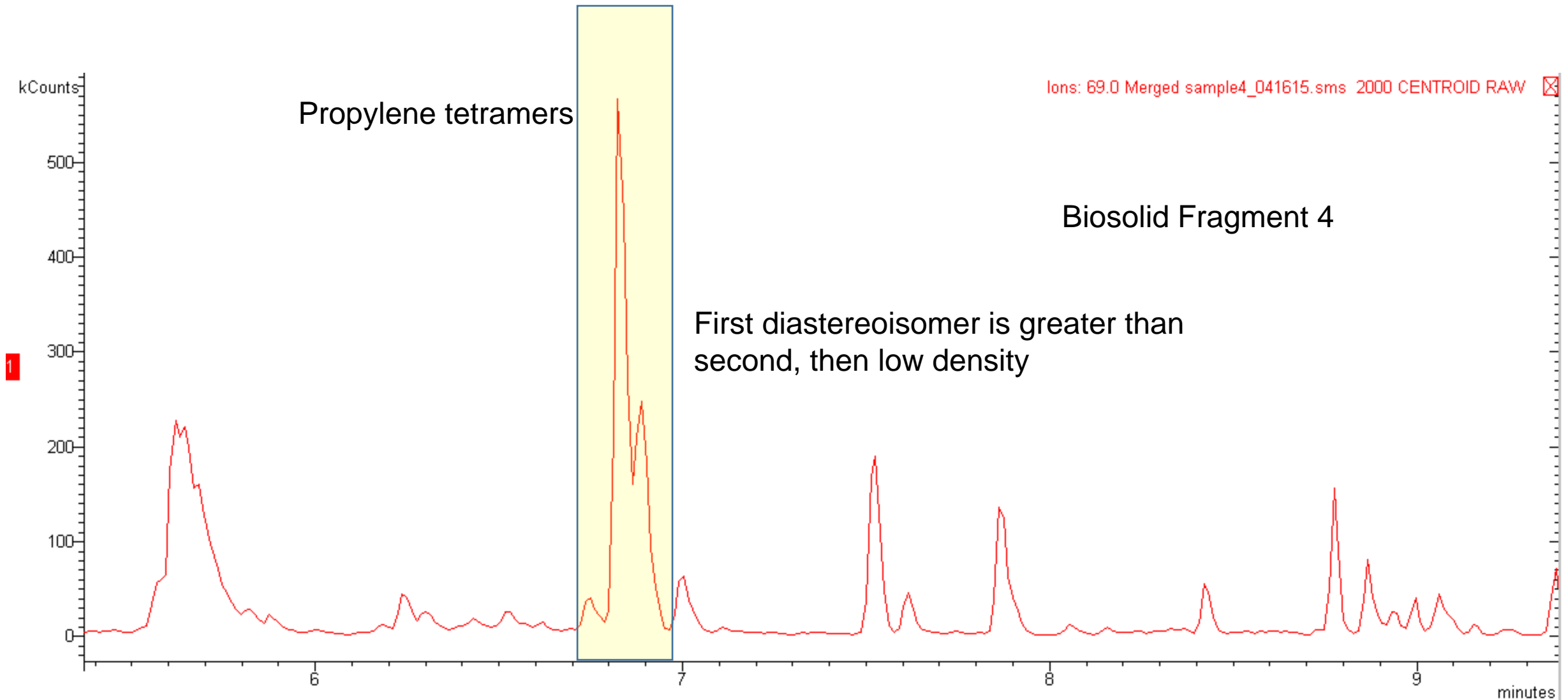
Propylene  
tetramers

Propylene  
pentamers

RIC Merged sample4\_041615.sms 2000 CENTROID RAW

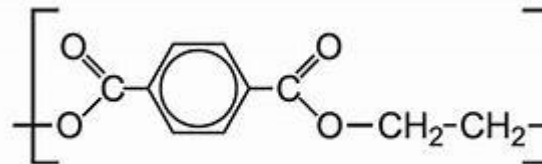


# Propylene Tetramers – Low Density versus High Density <sup>9</sup>



Moldoveanu, Serban. *Analytical pyrolysis of synthetic organic polymers*. Vol. 25. Elsevier, 2005.

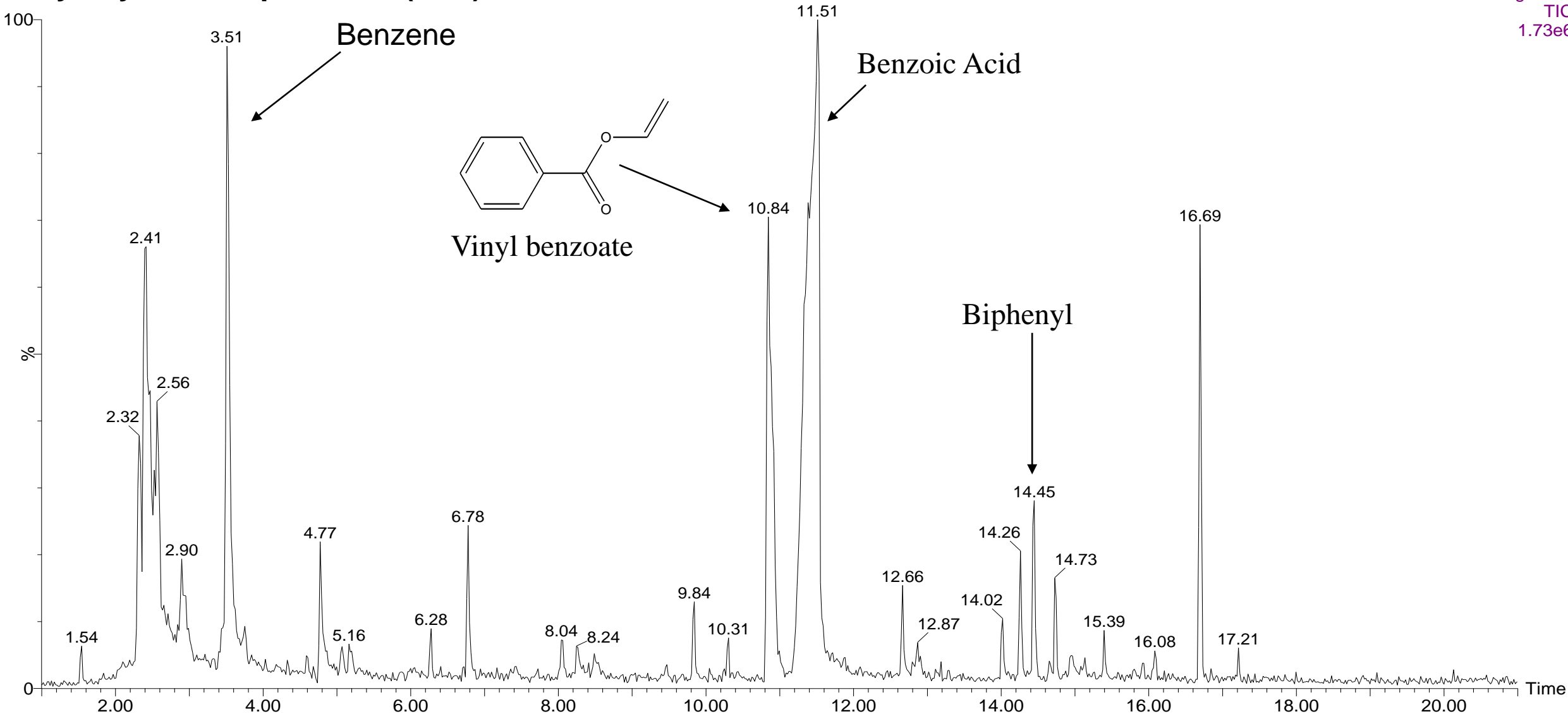
# Polyesters



#10

## Polyethylene terephthalate (PET)

Voltage EI+  
TIC  
1.73e6

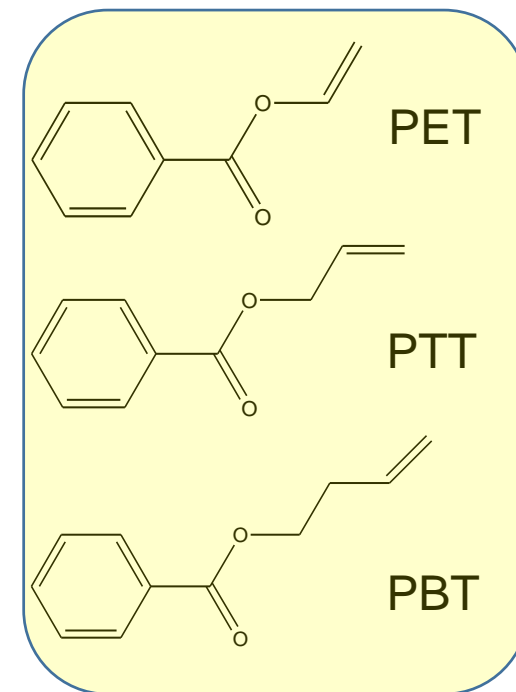
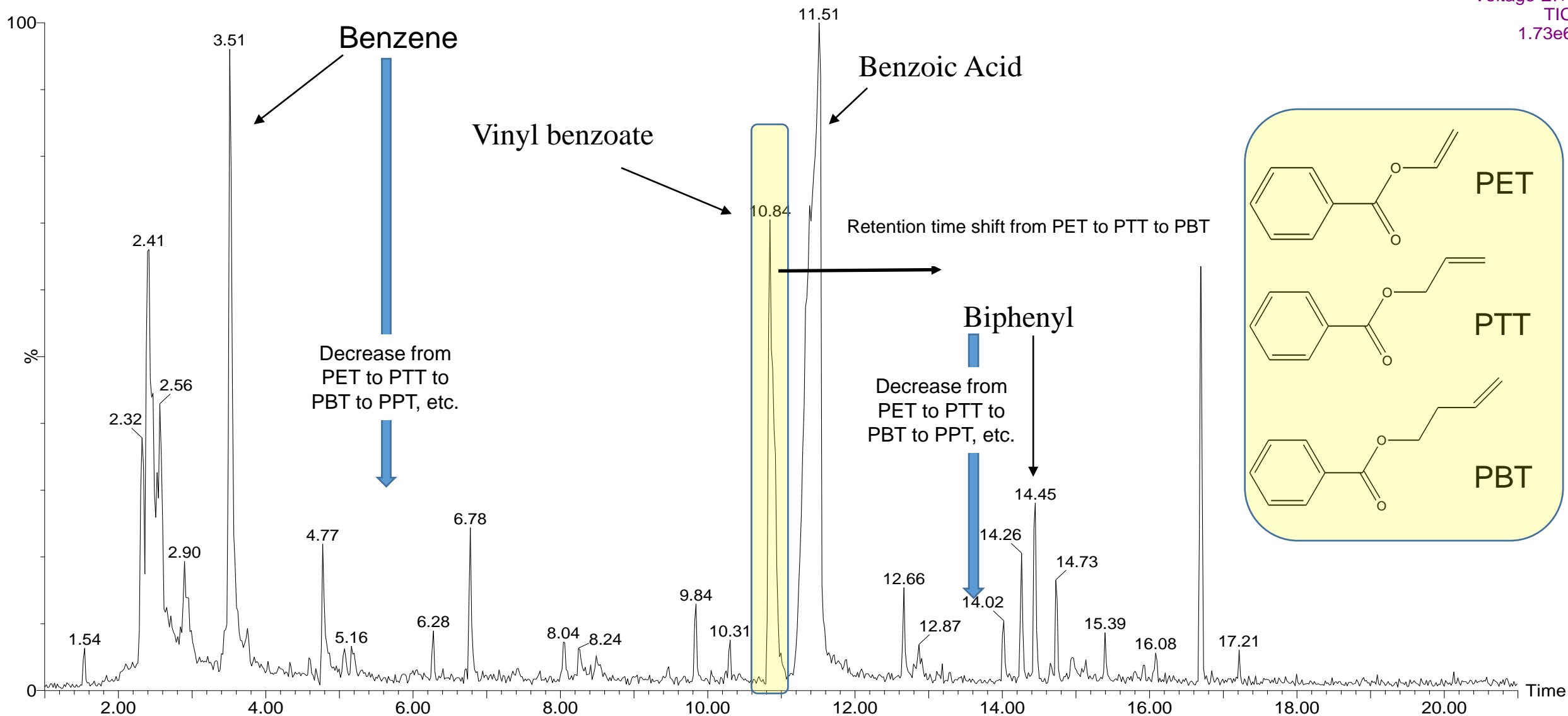


# Polyesters

#11

## Other forms

Voltage EI+  
TIC  
1.73e6





# Spectra Averaging to Facilitate Library Searching

12

AWRI\_Polypropylene\_B1\_031518

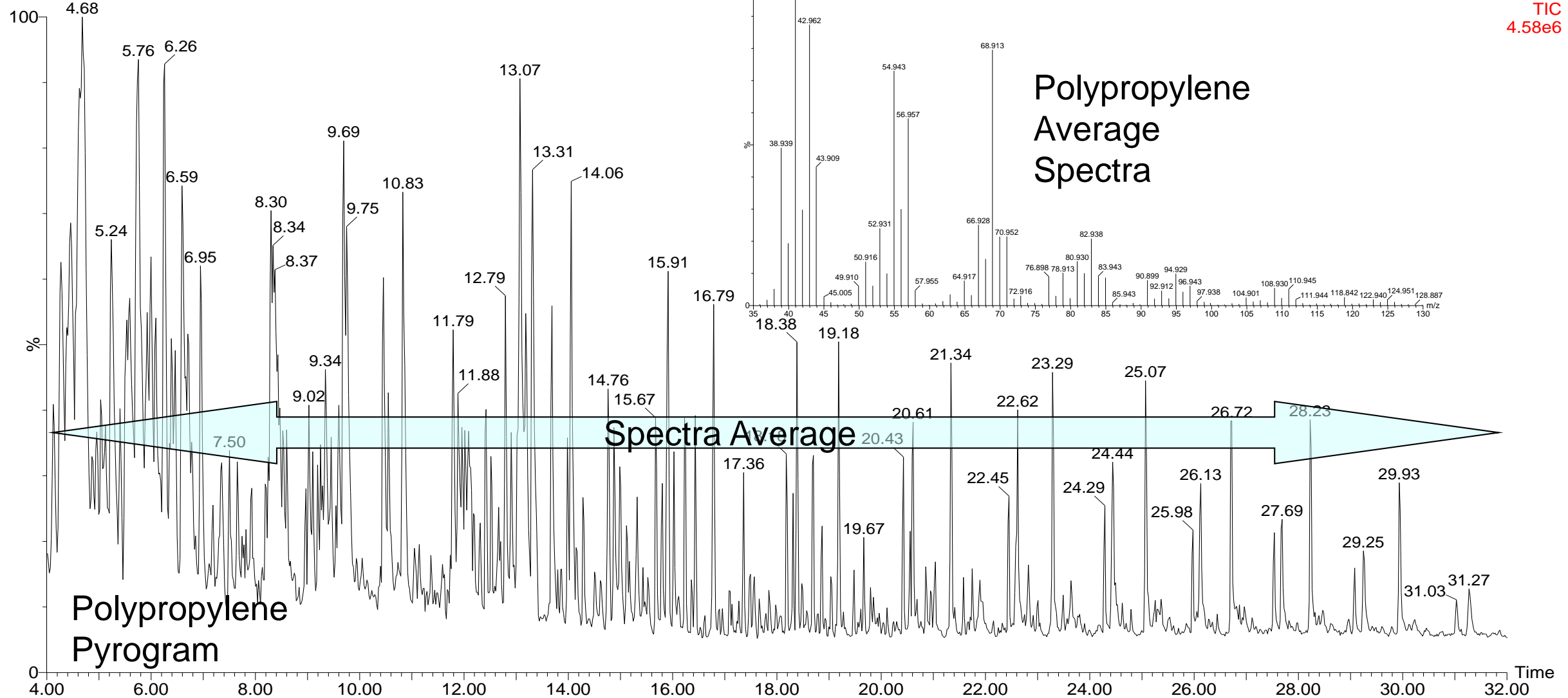
AWRI\_Polypropylene\_B1\_031518

AWRI\_Polypropylene\_B1\_031518

AWRI\_Polypropylene\_B1\_031518 252 (4.680) Cm (222:1706)

Voltage EI+  
8.52e4

Voltage EI+  
TIC  
4.58e6



# Database Searching of Pyrograms

13

NIST MS Search 2.0 - [Ident, Presearch Default - InLib = 160, 100 spectra]

File Search View Tools Options Window Help

Go 1. AWRI\_Polypropylene\_B1\_031518 25: [?] [?] [?] [?]

#	Src.	Name
1	A	AWRI_Polypropylene_B1_031518 252 (4.680) Cm (222:1706)
2	L	AWRI_POLYPROPYLENE_B1_031518SUBTRACT 252 (4.680) Cm (121:2046)
3	L	MB_PolyPropylene_031518 171 (3.175) Cm (113:2046)
4	L	PESTD_031218SUBTRACT 499 (9.264) Cm (498:499+508:515+492:495))
5	L	AWRI_LDPE_B1_031418SUBTRACT 248 (4.604) Cm (115:2047)
6	L	PESTD_031218SUBTRACT 443 (8.224) Cm (113:2047)
7	L	LUCSAMPLE17_011118SUBTRACT 345 (6.407)
8	L	LUCSAMPLE17_011118SUBTRACT 141 (2.618) Cm (2:833)
9	L	LUCSAMPLE11_010817SUBTRACT 400 (7.428)
10	L	LUCSAMPLE11_010817SUBTRACT 451 (8.375)
11	L	LUCSAMPLE11_010817SUBTRACT 322 (5.979)
12	L	LUCSAMPLE11_010817SUBTRACT 280 (5.200)
13	L	LUCSAMPLE11_010817SUBTRACT 189 (3.677)

Names Structures Spec List

#	Lib.	Match	R.Match	Prob. (%)	Name
1	mi	936	936	66.5	MB_PolyPropylene_031518 171 (3.175) Cm (113:2046)
2	mi	886	886	13.5	AWRI_POLYPROPYLENE_B1_031518SUBTRACT 252 (4.68...
3	mi	850	854	3.34	TAMPAXPOCKETPEARL_BLUEAPPART_112717SUBTRA...
4	mi	843	848	2.56	TAMPAXPOCKETPEARL_OUTSIDEWRAPPER_112917SUB...
5	mi	837	843	2.01	SLOT34_GP_POLYETHYLENE_110717SUBTRACT 1083 (20...
6	mi	836	841	1.93	MBPOLYPROPYLENE_101017SUBTRACT 710 (13.182) Cm (...)
7	mi	833	837	1.70	CLEARFILM_LUCFILTERS_101017SUBTRACT 129 (2.395) C...
8	mi	825	831	1.27	TAMPAXPOCKETPEARL_CLEARAPPART_112917SUBTR...
9	py	814	848	0.87	Rubber, Ethylene(78.6%)/Propylene
10	py	810	852	0.73	Rubber, Ethylene(54.2%)/Propylene
11	py	799	803	0.50	2-Ethyl hexyl acrylate
12	py	795	795	0.42	Adhesive, from clear tape
13	py	789	813	0.33	EPDM Rubber
14	py	782	801	0.25	Acrylic (2-EHA, 2-EHMA)
15	py	780	781	0.23	Paint (Styrene, acrylic, plasticizers)
16	py	778	791	0.21	Chewing gum, mint
17	mi	778	790	0.21	SLOT30_NYLON6_6_110117SUBTRACT 736 (13.664) Cm (5...

Names Structures InLib = 160, Hit List

Lib. Search Other Search Names Compare Librarian MSMS

For Help, press F1

Ident Ident

start gas chromatogrph... UoB\_Microplastics... MassLynx - AWRI ... Chromatogram - [...] Spectrum - [AWRI...] Windows Media Pl... NIST MS Search 2... 7:04 AM

Name: AWRI\_Polypropylene\_B1\_031518 252 (4.680) Cm (222:1706)  
MW: N/A ID#: 588 DB: Text File  
10 largest peaks:  
41 999 | 43 873 | 69 795 | 55 729 | 57 581 |  
39 490 | 44 430 | 56 299 | 42 297 | 67 251 |  
Synonyms:  
no synonyms.

(Text File) AWRI\_Polypropylene\_B1\_031518 252 (4.680) Cm  
Plot/Text of Search Spectrum Plot of Search Spectrum Plot/Text of Spec List

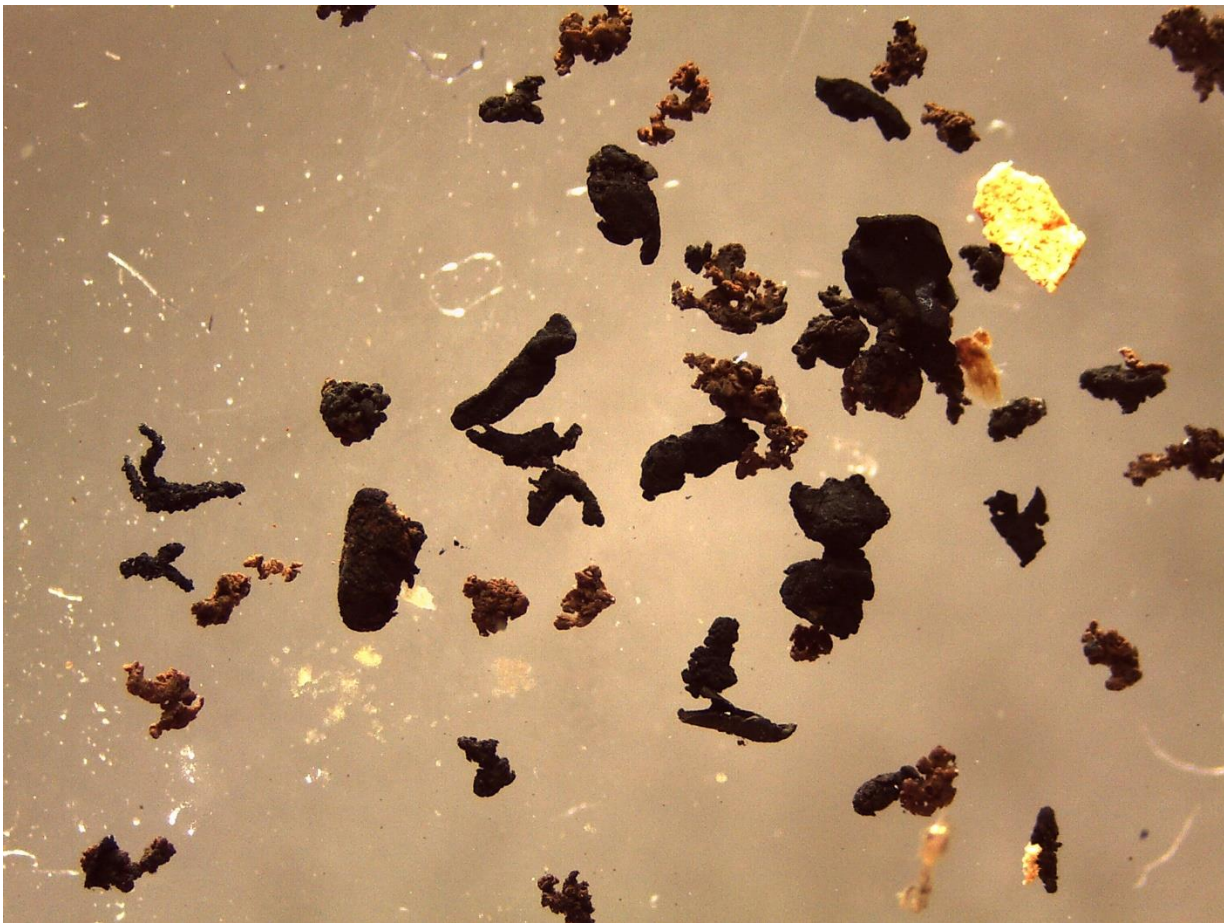
Name: MB\_PolyPropylene\_031518 171 (3.175) Cm (113:2046)  
MW: N/A ID#: 27 DB: microplastics\_2017  
10 largest peaks:  
41 999 | 43 922 | 69 857 | 55 739 | 57 621 |  
39 485 | 44 421 | 56 361 | 42 342 | 67 236 |  
Synonyms:  
no synonyms.

(microplastics\_2017) MB\_PolyPropylene\_031518 171 (3.175)  
Plot/Text of Hit Plot of Hit

# Examples: In-House Microplastics Database at ISTC

Ref #	Material
12	Kimberly Clark Purple Nitrile Glove
13	Tampax Pocket Pearl - Blue Applicator
14	Tampax Pocket Pearl - Inside White Absorbant
15	Tampax Pocket Pearl - Clear Part of Applicator
16	Tampax Pocket Pearl - Wrapper
17	Polylactic Acid from Clear Cup Plastic #7
18	Lube from Basic Condom
19	Whole Condom Right Out of Package
20	Basic Condom Outside Wrapper
21	Basic Condom Whole, lube extracted
22	Polycarbonate from CD

# The Mystery Material – Black Flakes

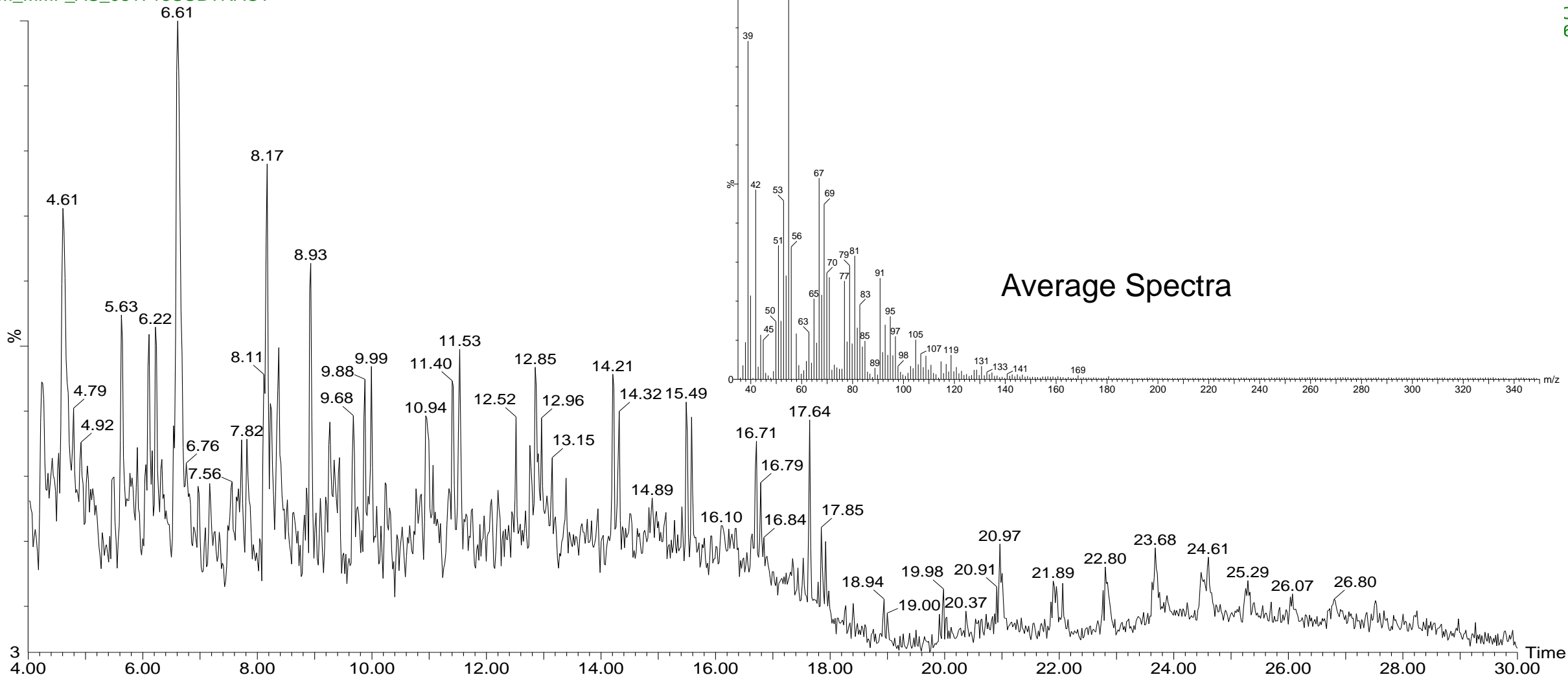


Photos and Materials Courtesy of Sherri Mason and Peter Lenaker



# Mystery Black Flake – Pyrogram / Average Spectra

SM\_MMF\_AS\_081718  
SM\_MMF\_AS\_081718SUBTRACT

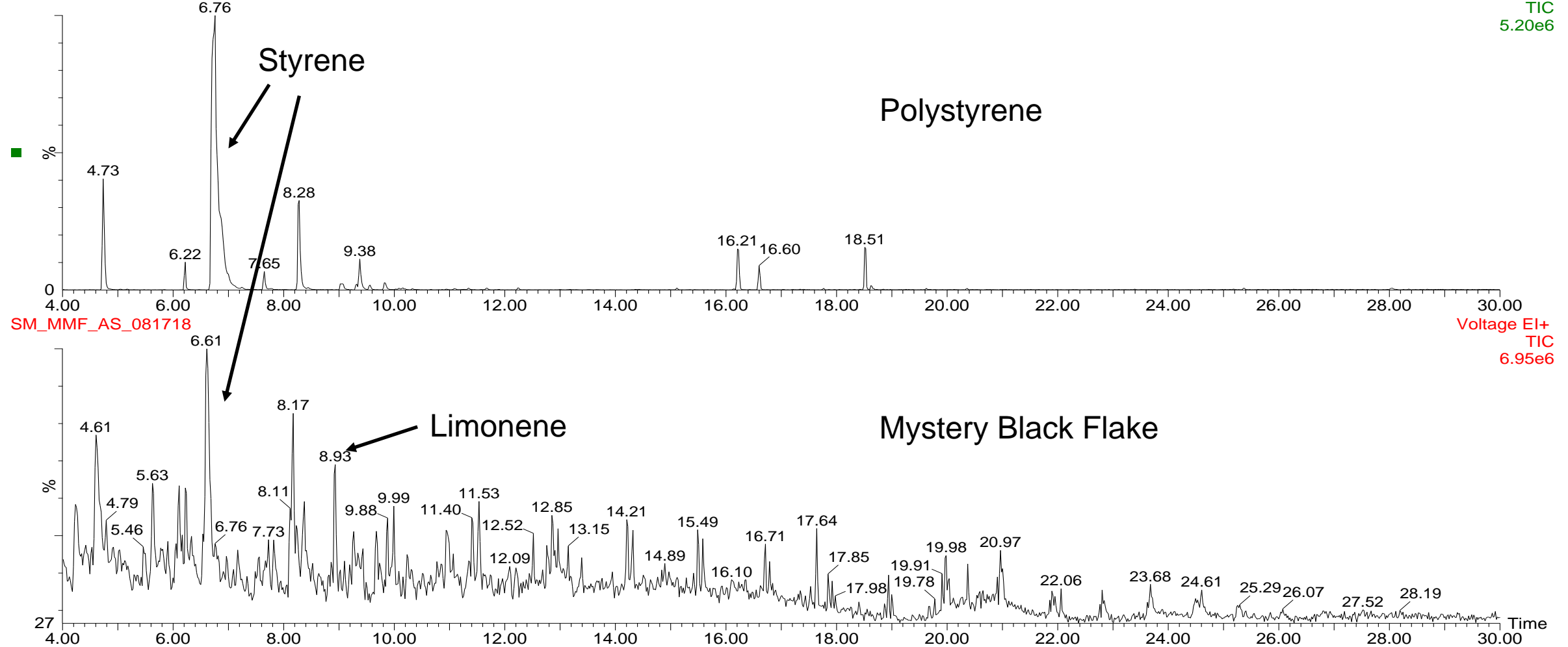


# Mystery Black Flake Pyrogram– A Deeper Look

polystyrene6\_101017

POLYSTYRENE6\_101017SUBTRACT

Voltage EI+  
TIC  
5.20e6



# Common Pyrolysis products of Styrene-butadiene<sup>18</sup><sup>5</sup>

- Xylenes
- Toluene
- Styrene
- Limonene
- Propylbenzene
- Butadiene trimers (BBB) – Accurate Mass 162.1409
- Styrene-butadiene dimers (SB) – Accurate Mass 158.1096
- Styrene-butadiene-butadiene trimers (SBB) - Accurate Mass 204.0939

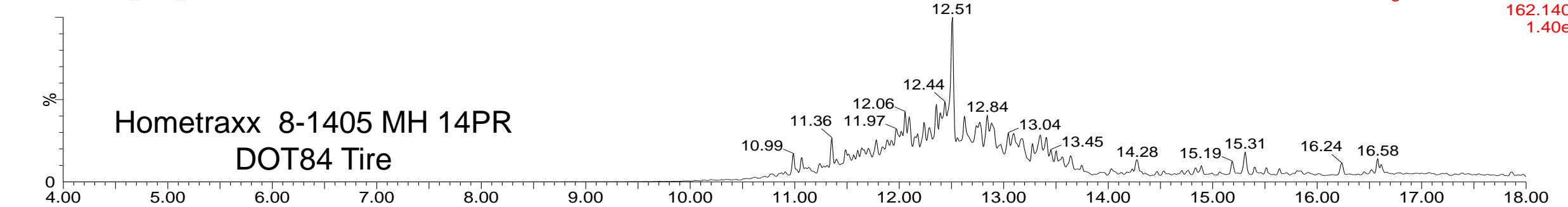
5- Tsuge, Shin, Hajima Ohtani, and Chuichi Watanabe. *Pyrolysis-GC/MS data book of synthetic polymers: pyrograms, thermograms and MS of pyrolyzates*. Elsevier, 2011.

# High Resolution Pyrogram - Mass 162.1409 (BBB Trimer)

MMFAS\_HR1\_082019

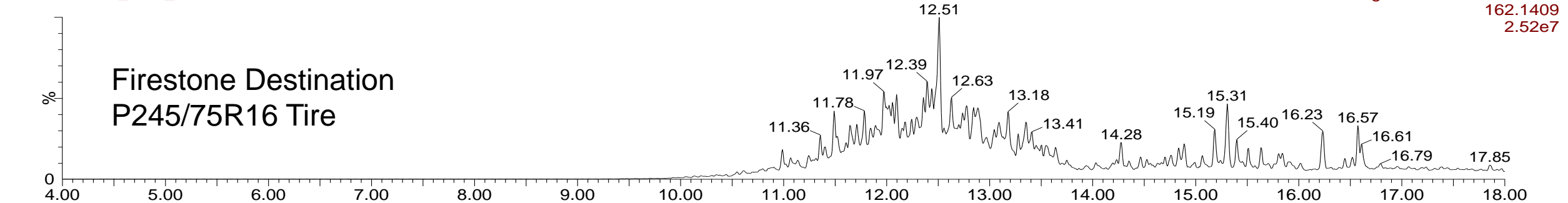
HometraxxTire\_HR1\_082118

Voltage SIR 4 Channels EI+  
162.1409  
1.40e8



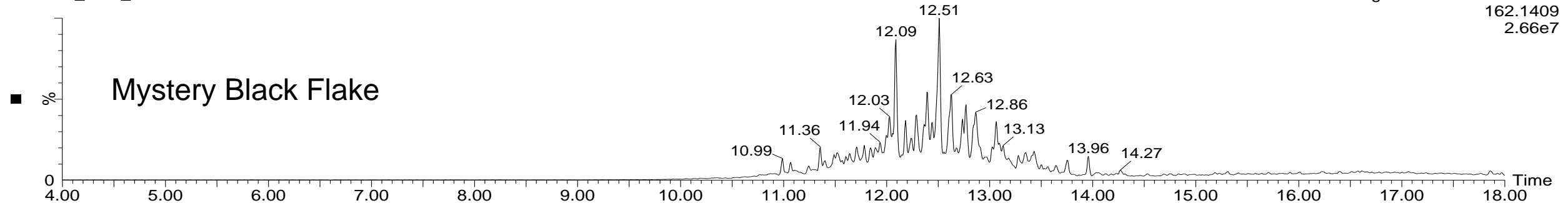
FireStoneTire\_HR1\_082118

Voltage SIR 4 Channels EI+  
162.1409  
2.52e7



MMFAS\_HR1\_082019

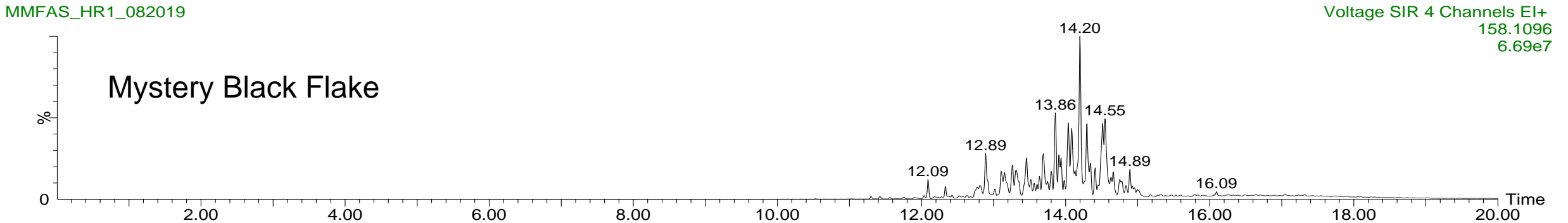
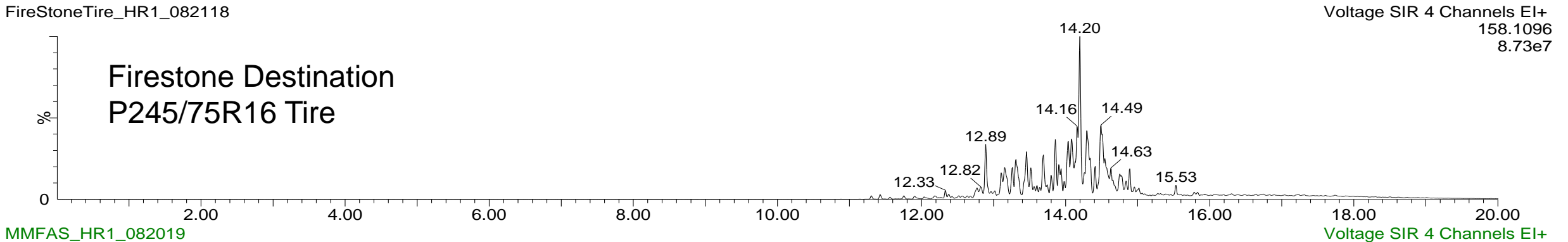
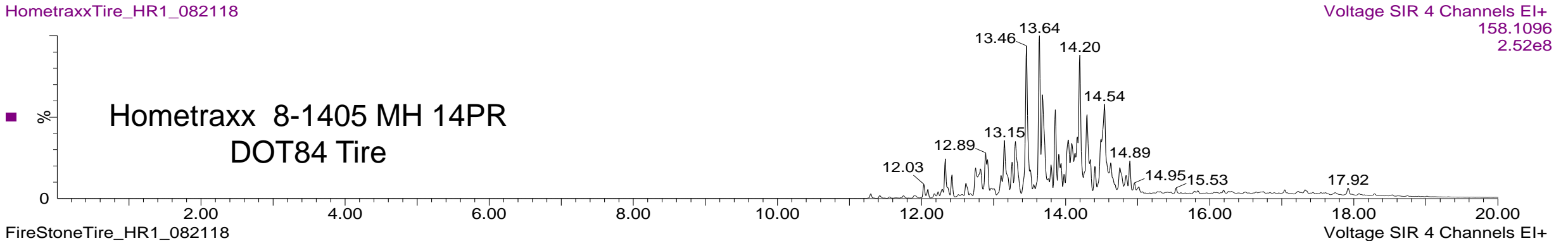
Voltage SIR 4 Channels EI+  
162.1409  
2.66e7





# High Resolution Pyrogram - Mass 158.1096 (SB Dimer)

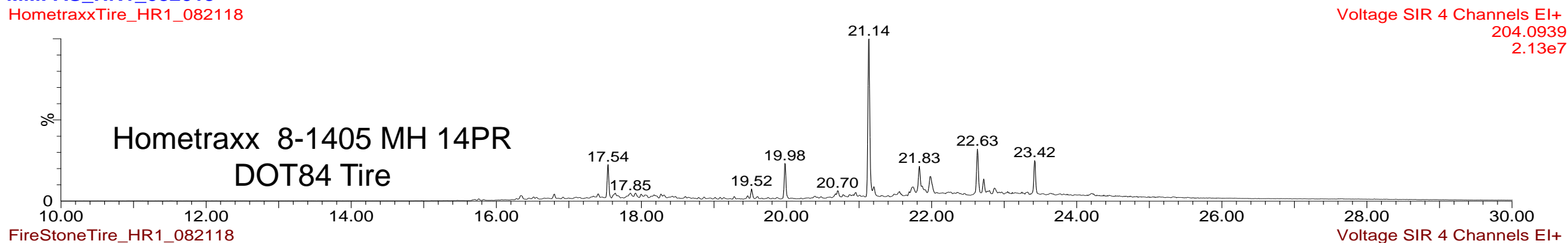
HometraxeTire\_HR1\_082118  
HometraxeTire\_HR1\_082118



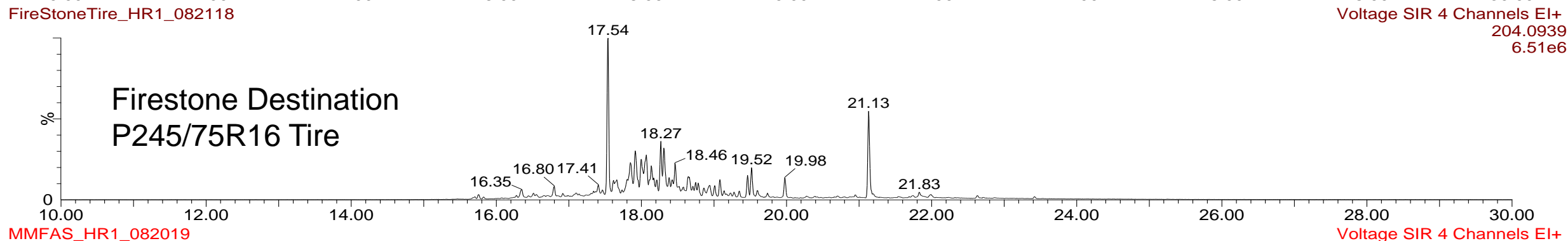
# High Resolution Pyrogram - Mass 204.0939 (SBB Hybrids)

MMFAS\_HR1\_082019

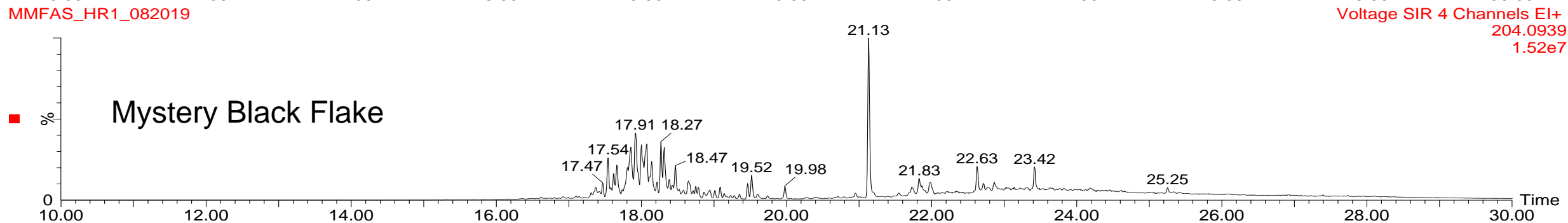
HometraxeTire\_HR1\_082118



FireStoneTire\_HR1\_082118

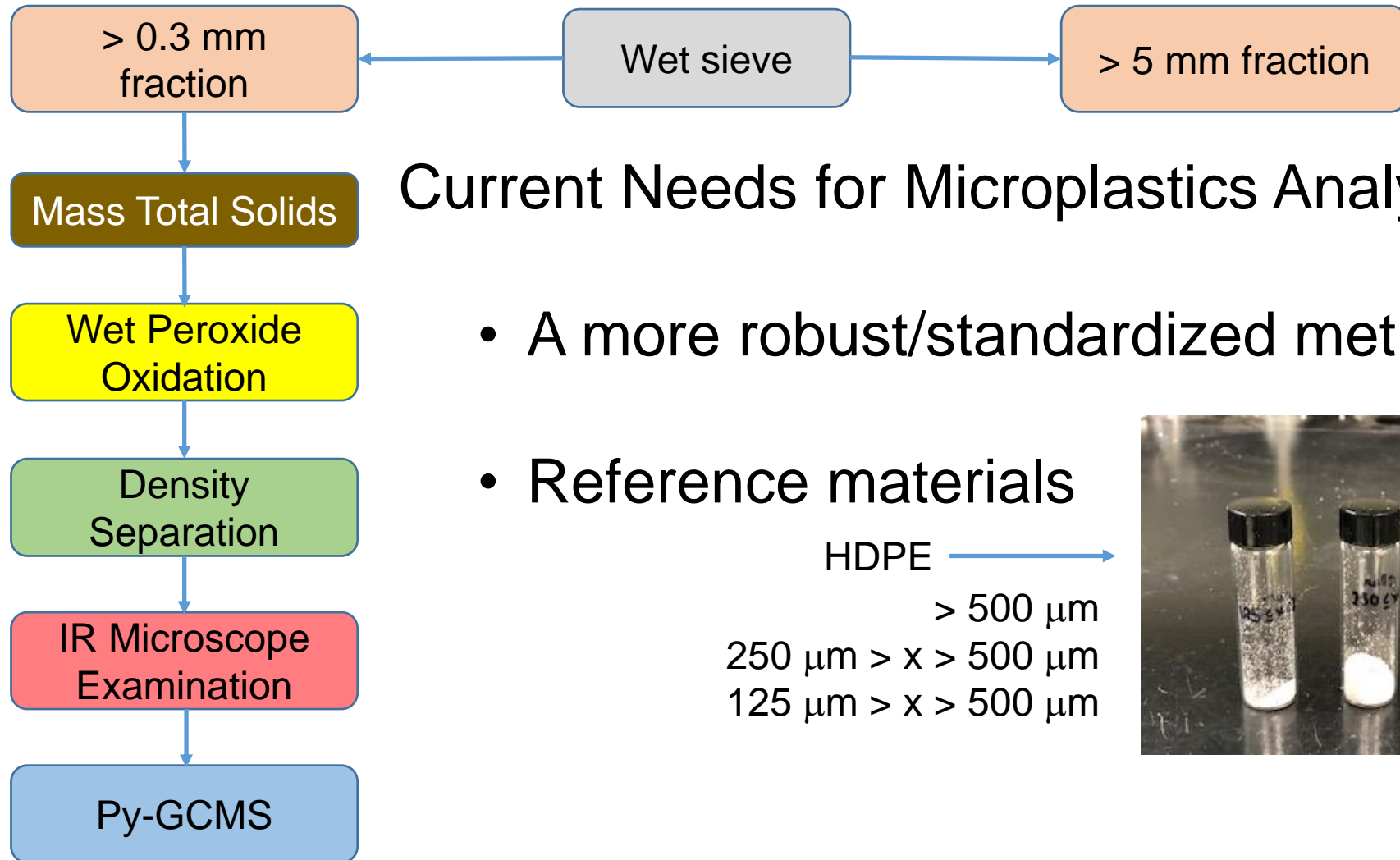


MMFAS\_HR1\_082019



# Standard Method for Analysis of Microplastics – Waters<sup>6</sup>

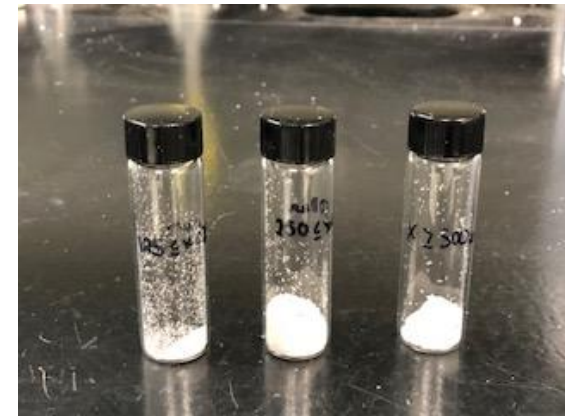
22



## Current Needs for Microplastics Analysis

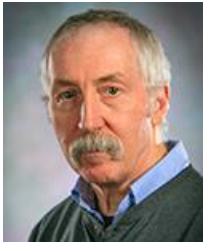
- A more robust/standardized method
- Reference materials

HDPE →  
> 500 μm  
250 μm > x > 500 μm  
125 μm > x > 500 μm



6- Masura, Julie, Joel E. Baker, Gregory Duane Foster, Courtney Arthur, and Carlie Herring. "Laboratory methods for the analysis of microplastics in the marine environment: recommendations for quantifying synthetic particles in waters and sediments." (2015).

# Acknowledgments - Collaborators



Sam Panno –  
Illinois Geological  
Survey



Rae McNeish  
California State  
University



Alan Steinmann  
Annis Water  
Resources Institute



Stuart Harrad  
University of  
Birmingham



Iseult Lynch  
University of  
Birmingham



Tim Leon ISTC

23

Walt Kelly– Illinois  
State Water Survey



John Kelly– Loyola  
University Chicago



Peter Lenaker–  
United States  
Geological Survey



Sherri Mason  
Fredonia New York



Maggie Oudsema  
Annis Water  
Resources Institute



Nancy Holm  
ISTC



Mohamed  
Abdallah  
University of  
Birmingham



Kathryn  
Gunderson ISTC



Jessica Porter  
ISTC



Tim Hoellein– Loyola  
University Chicago



-Rick Rediske  
Annis Water  
Resources Institute



Lee Green  
ISTC



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- Illinois Indiana Sea Grant (NA18OAR4170082)
- University of Illinois Professional Development Fund

# From microplastics to per & polyfluoroalkyl substances (PFAS)

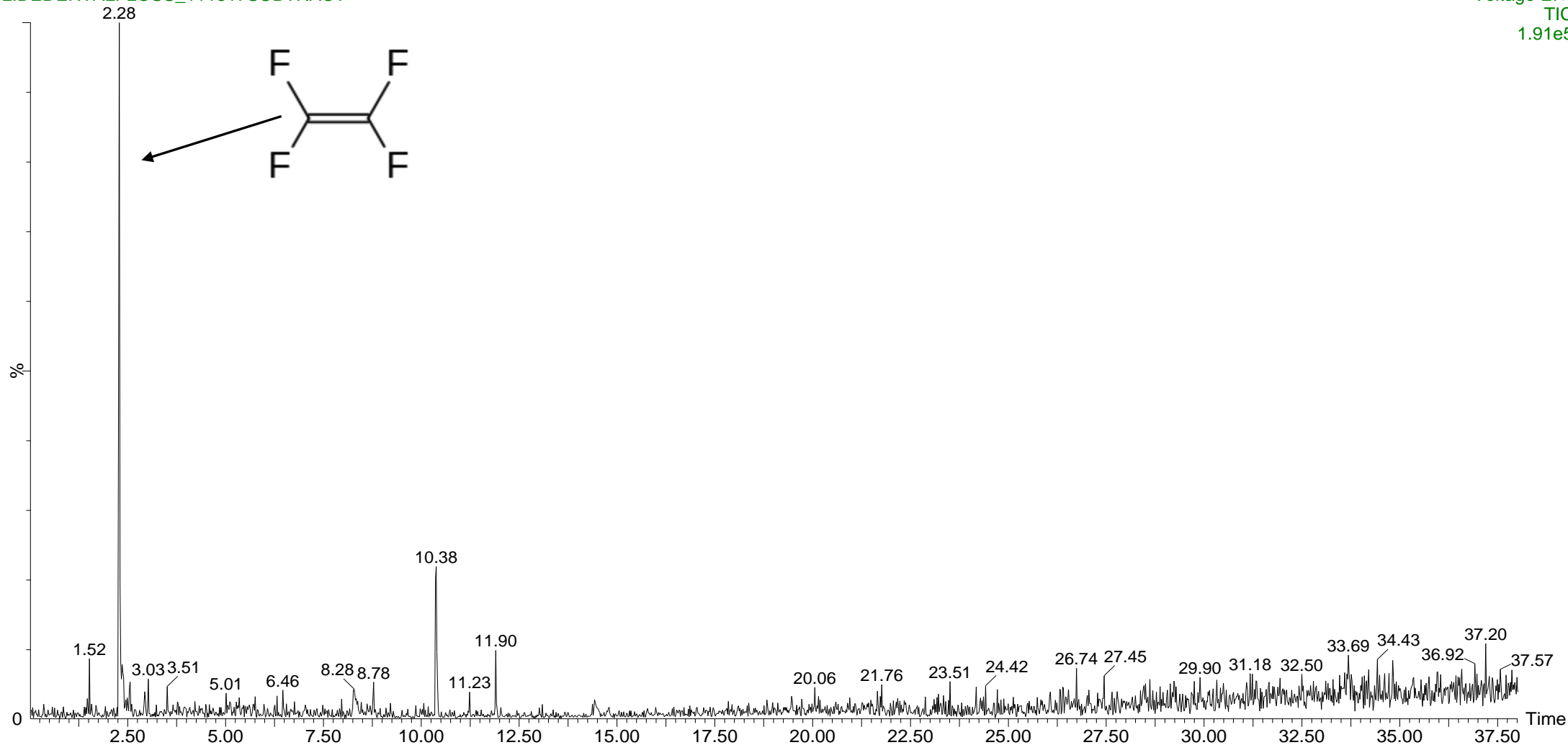
A potential py-GCMS application for screening of PFAS  
using total organic fluorine

# Dental Floss - Pyrogram

GlideDentalFloss\_111517

GLIDEDENTALFLOSS\_111517SUBTRACT

Voltage EI+  
TIC  
1.91e5

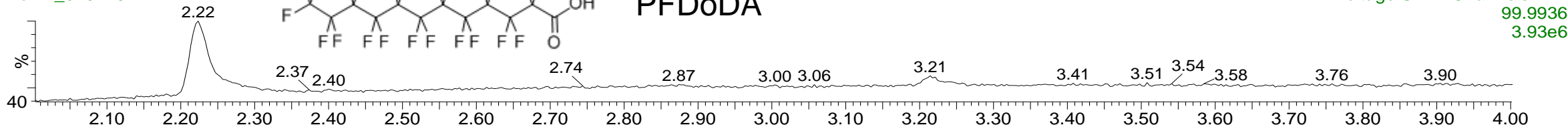


# Per & Polyfluoroalkyl Substances (PFAS)

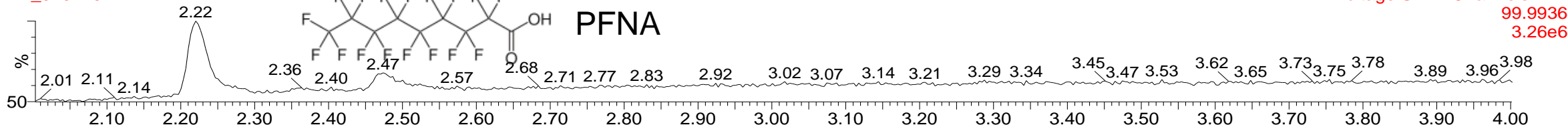
27

PFOS\_040219

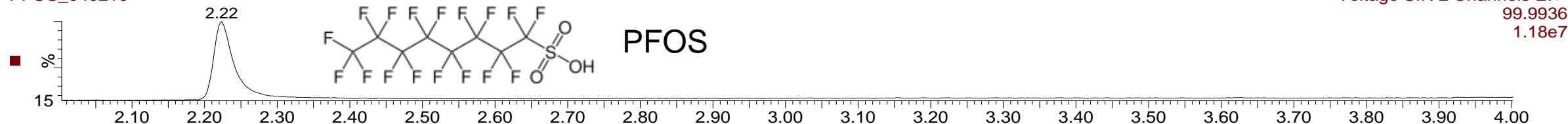
PFDoDA\_040219



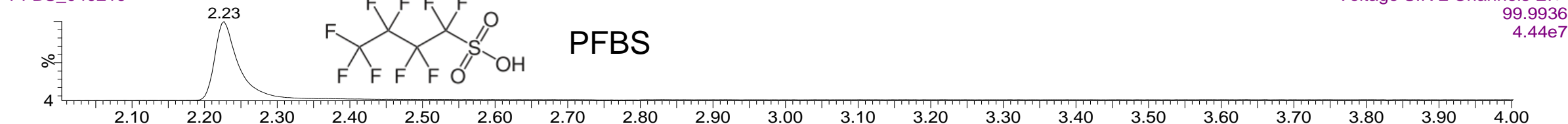
PFNA\_040219



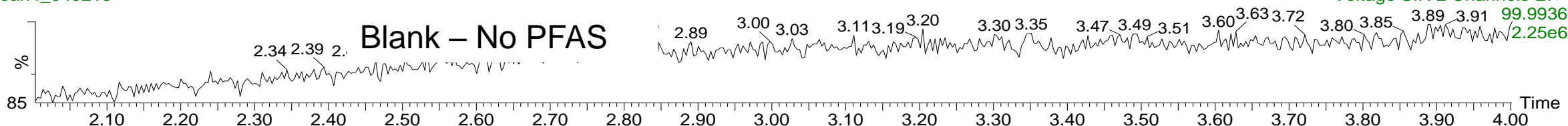
PFOS\_040219



PFBS\_040219



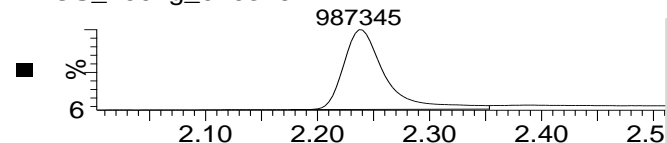
Clean4\_040219



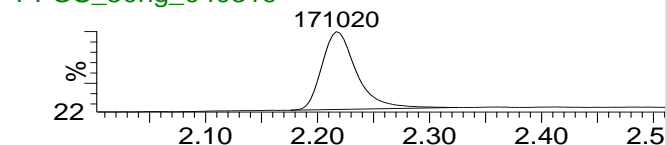
# Calibration with PFOS

PFOS\_50ng\_040319

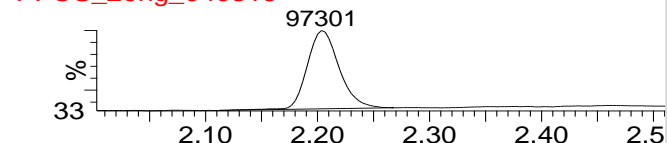
PFOS\_200ng\_040319



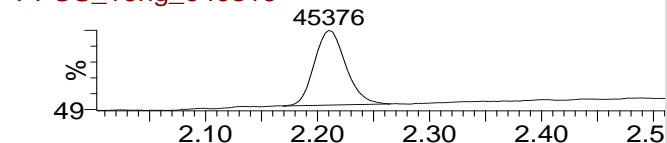
PFOS\_50ng\_040319



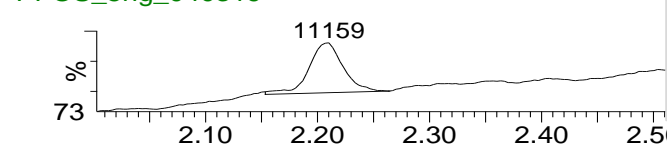
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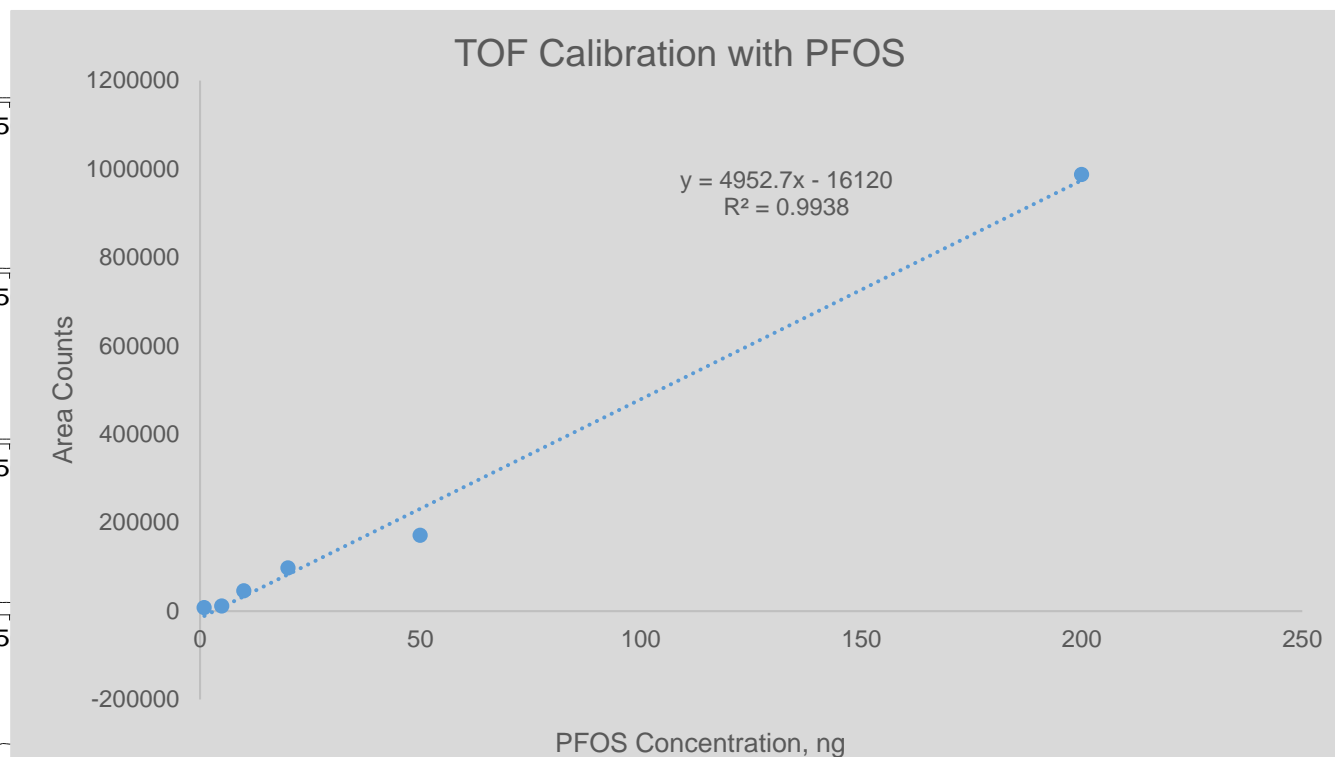
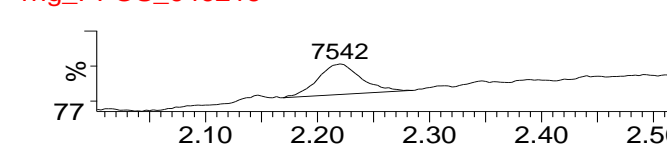
PFOS\_10ng\_040319



PFOS\_5ng\_040319



1ng\_PFOS\_040219



Voltage SIR 2 Channels EI+

99.9936

2.46e7

Area

Voltage SIR 2 Channels EI+

99.9936

6.36e6

Area

Voltage SIR 2 Channels EI+

99.9936

4.49e6

Area

Voltage SIR 2 Channels EI+

99.9936

2.97e6

Area

Voltage SIR 2 Channels EI+

99.9936

1.90e6

Area

Voltage SIR 2 Channels EI+

99.9936

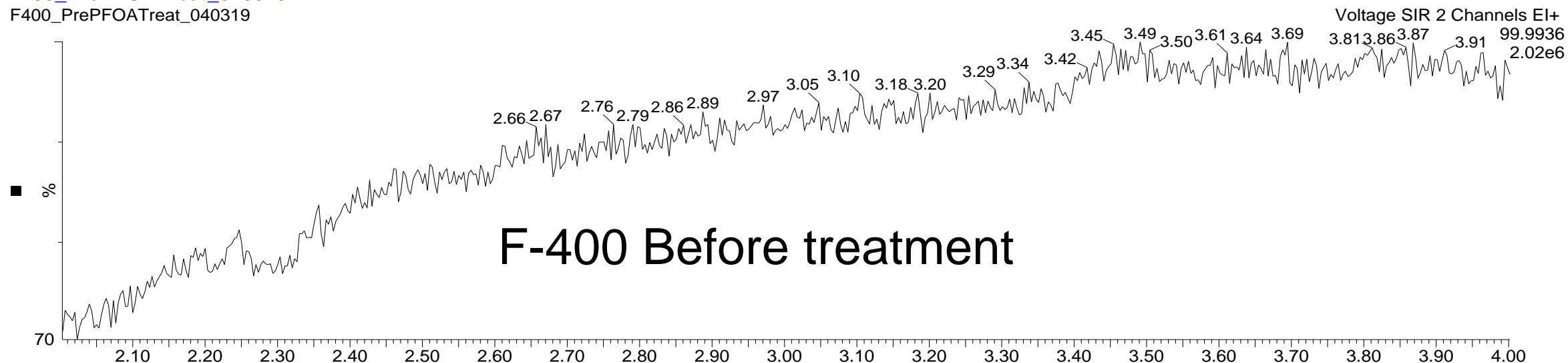
1.94e6

Area

# Total Organic Fluorine – Activated Carbon

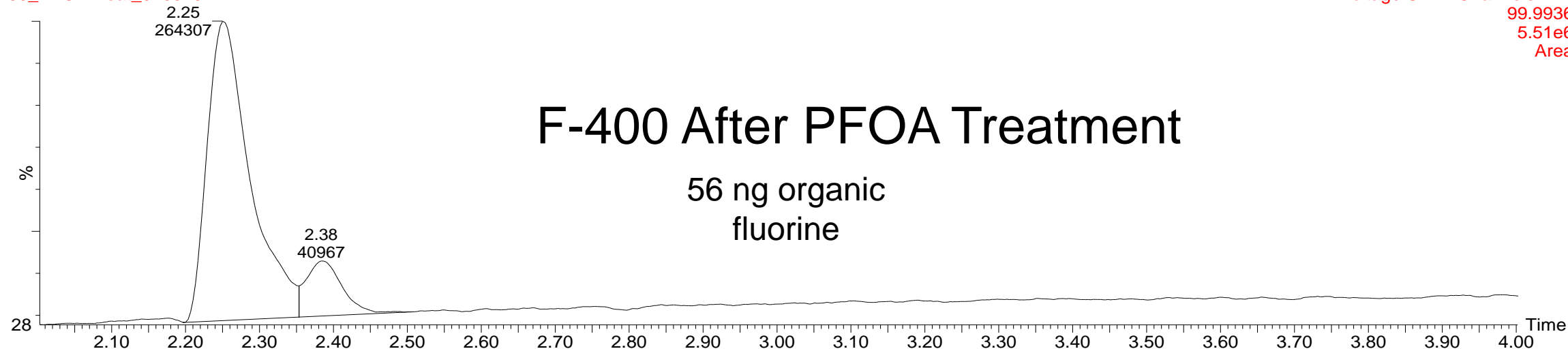
F400\_PrePFOATreat\_040319

F400\_PrePFOATreat\_040319



F-400 Before treatment

F400\_PFOATreat\_040319



F-400 After PFOA Treatment

56 ng organic  
fluorine



# Questions?



John W Scott, ISTC Senior Analytical Chemist

[zhewang@Illinois.edu](mailto:zhewang@Illinois.edu)

217-333-8407

